Sustainable Hydrogen and Electrical Energy Storage
5

Interested in H_2 (again)

De Telegraaf DFT.nl nieuws

Foto: ANP
za 11 mei 2013, 09:55

Shell ziet weer toekomst in waterstof

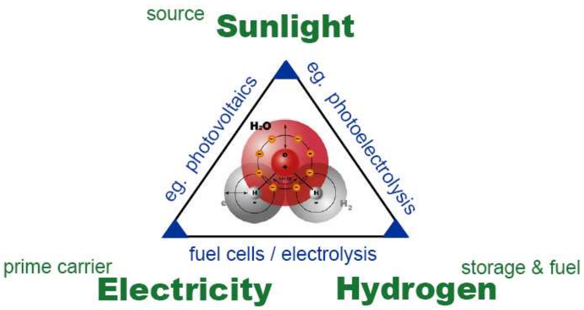
DEN HAAG (AFN) - Olie- en gasproducent Shell wil waterstof een nieuwe kans geven. Door technologische ontwikkelingen en nieuwe toepassingen voor waterstof lijkt de productie ervan rendabeler te worden. Dat zegt president-directeur van Shell Nederland Dick Benschop in De Telegraaf.

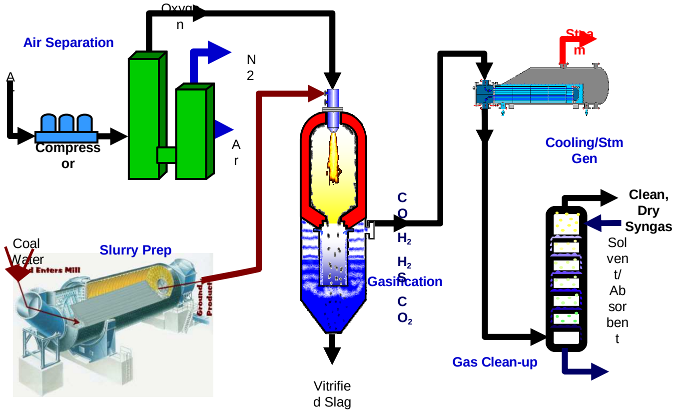
,,Tien jaar geleden waren we te vroeg, nu ziet de wereld er anders uit'', verklaart de topman de ommezwaai van zijn concern. Begin deze eeuw stopte Shell nog met zijn investeringen in de ontwikkeling van waterstofinstallaties.

Mail Print
DFT Nieuwsbrief
Proefabonnement,

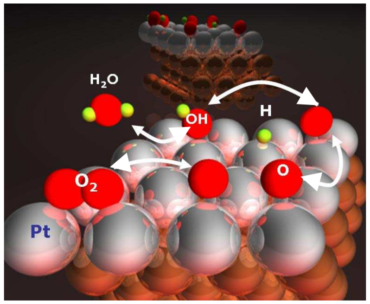
F.M. Mulder & M. Wagemaker

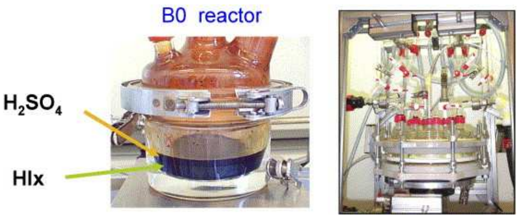
Previously: hydrogen production.






Source: Ernst Moritz Arndt University



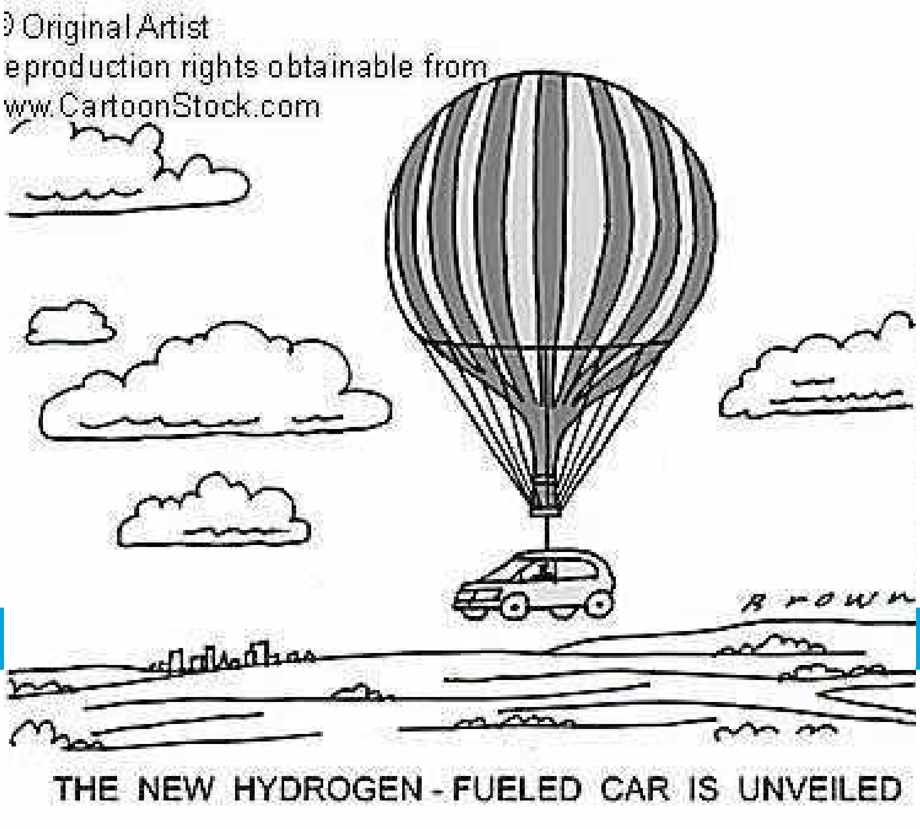


Now we need its transport, delivery, storage

- gas cylinders
- liquid
- pipelines
- surface adsorption materials
- metal hydrides

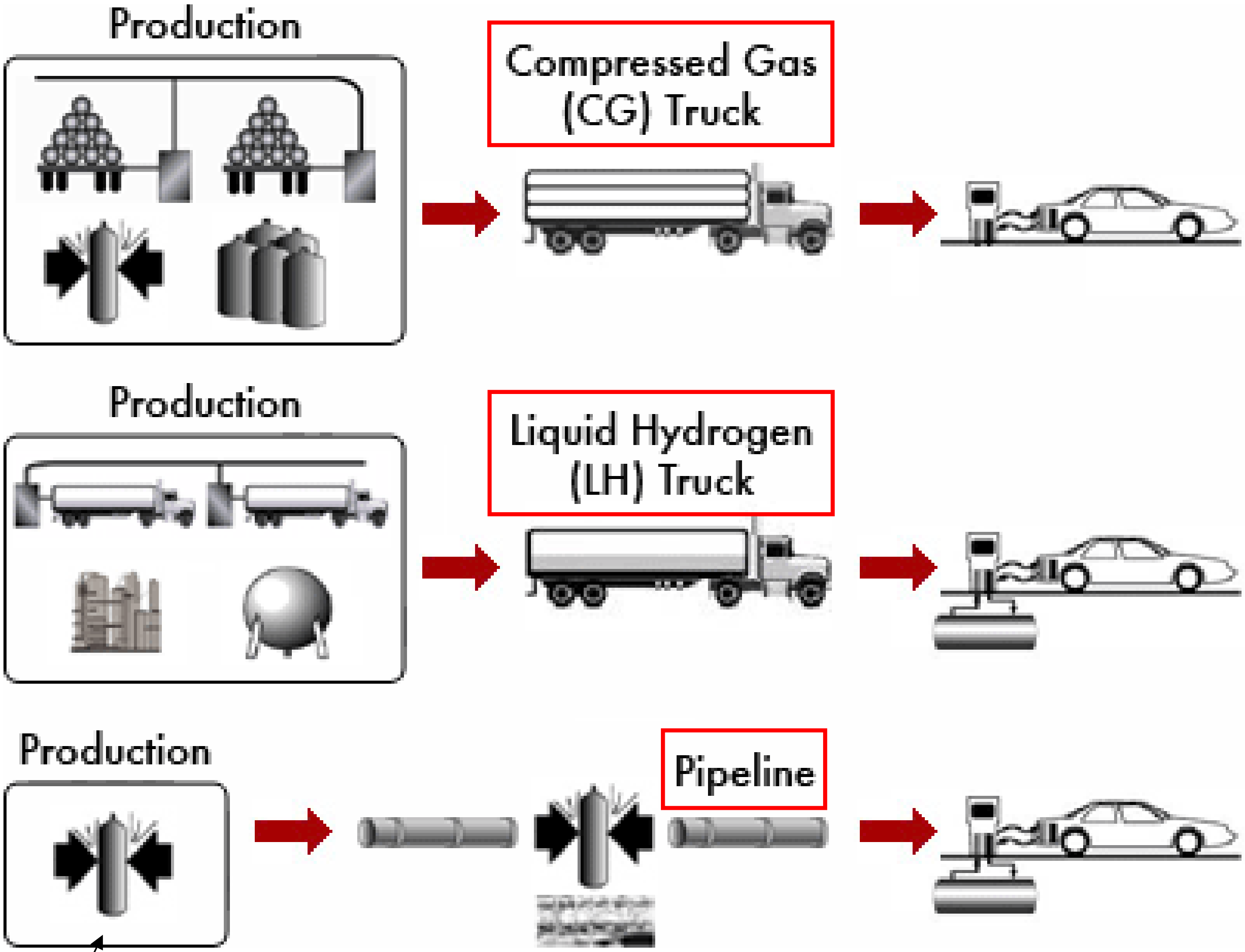
Main currently used technologies

research



THE NEW HYDROGEN-FUELED CAR IS UNVEILED

Hydrogen delivery, currently used technologies Gupta 10.1-10.2



compression

Hydrogen delivery over some larger distance is
currently limited to transport from production site
to e.g. refineries and other consumers:

Only some 700 mile of transport pipeline is present in the US.

Renewable energy related pilot study: GE Global Research

GE Global Research
Pilot study

H_2 Production - Pipeline Delivery (Tug Hill -Syracuse)

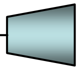
500 MW
\$1000/kW
η ~ 40%

200 MW

4500kg (150 MWh)
\$100/kWh
η ~ 99%

Hydrogen
Buffer Storage

350 bar

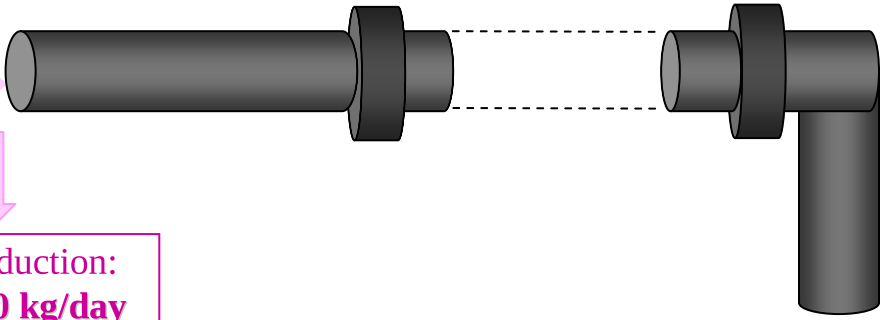


6 MW
\$1000/kW
η ~80%

200 MW
\$1000/kW
η ~75%

4500 kg/hr, 25 bar

Plateau-Syracuse: 30 miles
Hydrogen pipeline
10” Diameter, 25 bar
\$1M /mile
η ~99% (30 miles)



H_2 production:
108,000 kg/day
@ \$3.4/kg

O_2 Gas

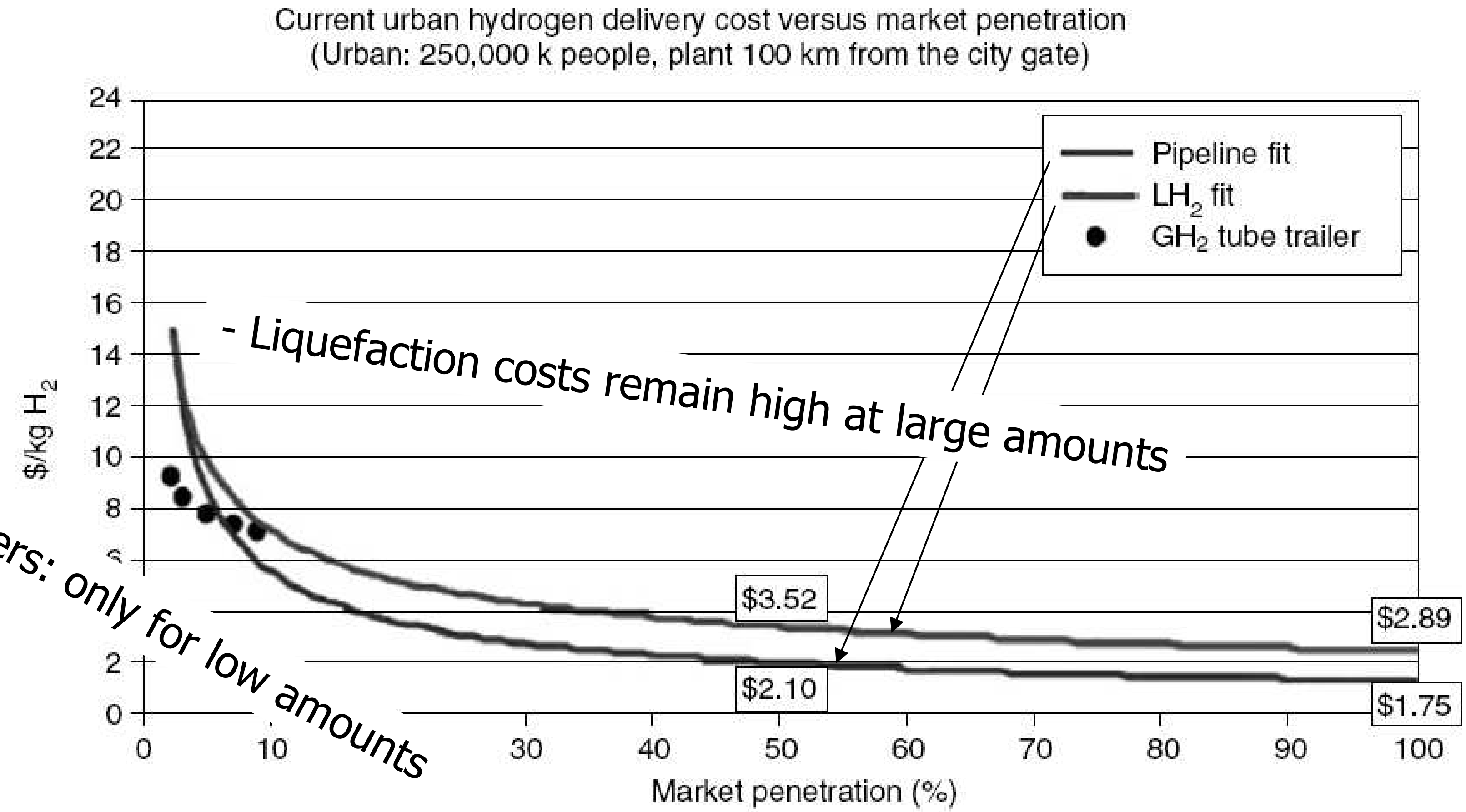
3 gal/kg H_2

Water Consumption
324,000 gal/day

H_2 production:
107,000 kg/day
@ \$3.5/kg

Major issues for hydrogen delivery:

- Pipelines: High initial investment costs
- All modes:
  - Materials issues: hydrogen embrittlement
  - Hydrogen leakage and monitoring
  - Hydrogen pressurizing/compression
- Liquid hydrogen: liquefaction costs and low temperatures



- Liquefaction costs remain high at large amounts

Trailers: only for low amounts

~ Amount of H_2 delivered

FIGURE 10.3
H2A delivery scenario model for H_2 delivery to urban market (250,000 people).

H2A: ‘hydrogen analysis’ program of DOE

Hydrogen delivery, lowest cost mode of current methods

The lowest-cost mode varies with distance and the amount of hydrogen delivered.

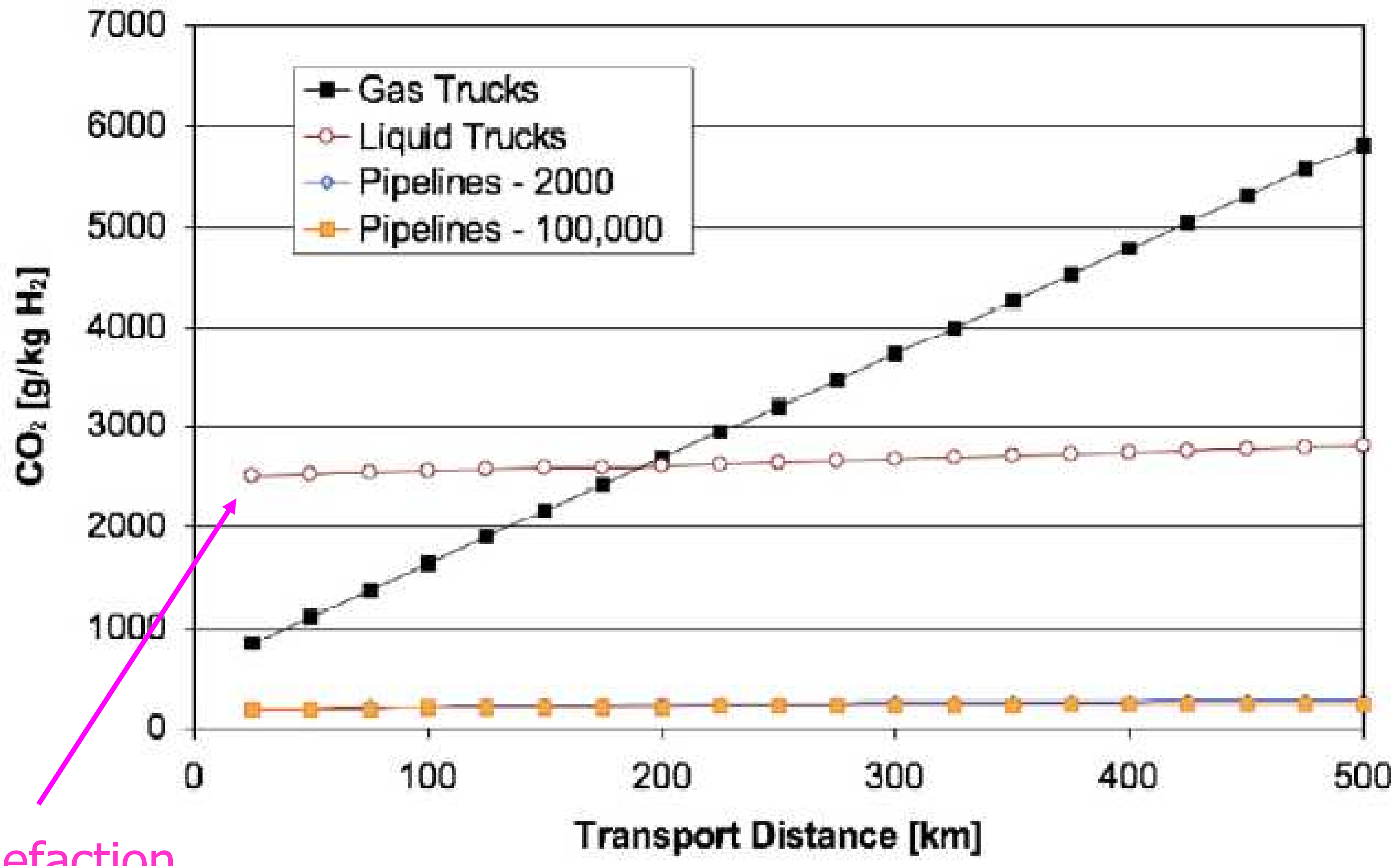
- For short distances and small amounts, gas trucks are preferred. Main costs: capital costs for trucks and trailers, labour costs, and fuel costs. Costs scale linearly with delivery distance and number of trucks/amount.

- For medium amounts of hydrogen and long distances, Liquid H_2 truck delivery is preferred. Largest cost factors: liquefaction equipment capital costs and electricity for liquefaction. For 100km the pipeline is cheaper fig 10.3.

- For large amounts of hydrogen: pipeline transmission is preferred. The pipeline capital cost is the largest single factor. Pipeline costs scale strongly with both distance and flow rate.

See paper: C. Yang, J. Ogdena; Determining the lowest-cost hydrogen delivery mode, International Journal of Hydrogen Energy 32 (2007) 268 – 286

Hydrogen delivery costs, expressed in fossil fuel CO_2 emission*



Liquefaction
initial costs
also at 0 km

* so this is essentially an energy costs, *not* capital cost of the initial investment. Sorry for the funny unit…

This is a strange unit:

1000 g CO_2 /kg H_2 = CO_2 kg/kg H_2
But Mass CO_2 / Mass H_2 = (12+32) / 2 = 22 / 1

So number of CO_2 molecules /H_2 molecules:

1000 CO_2 g/kg H_2 = 1/22 x CO_2 molecule / H_2 molecule

So 6000 would be 6/22 CO_2 per H2 delivered…

Pipelines for hydrogen transport

- similar to natural gas pipeline systems
- Pumping station every 100 – 150 km

Main issue with pipelines:
the materials should be able to handle the presence of hydrogen. Normal pipelines made of steels, however, are not perfect! Why?

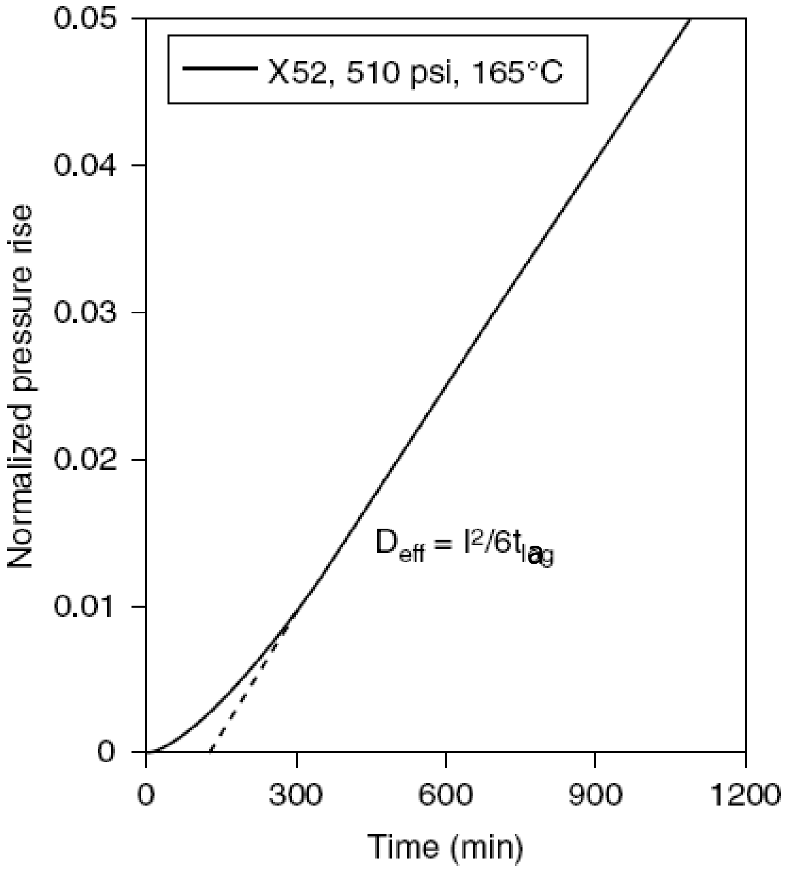
Hydrogen embrittlement.

Permeation of H2 through steels

Apply hydrogen pressure P_0 on one side of 1mm steel foil, and measure pressure rise P/P_0 at other side: this P stems from the H permeation through the material.

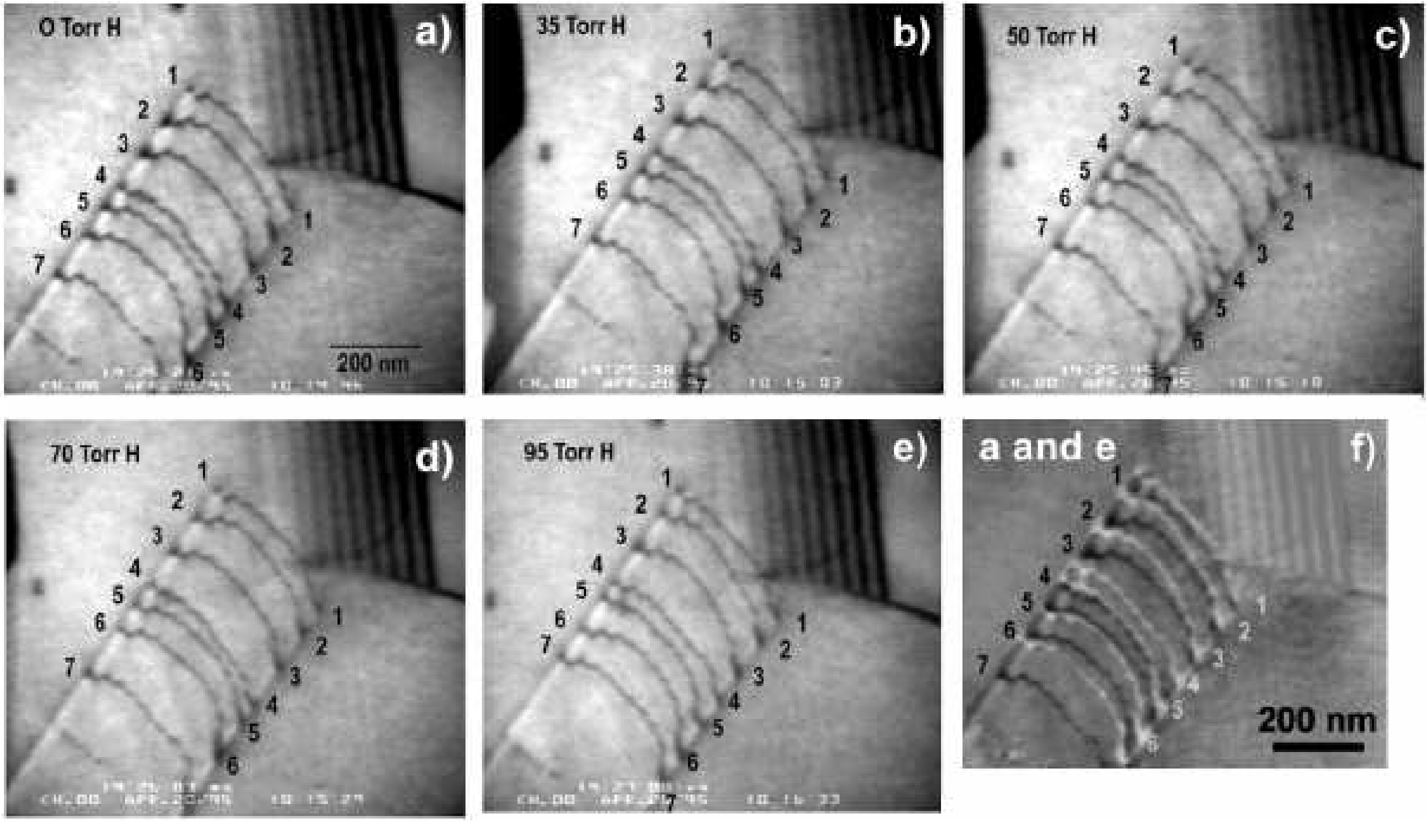
The rate of P increase is dependent on the H content inside the steel. This appears to become constant after some time > 300 min here.

The thickness l and time t_{lag} after which the P increase rate is constant can be used to determine a H diffusion coefficient.



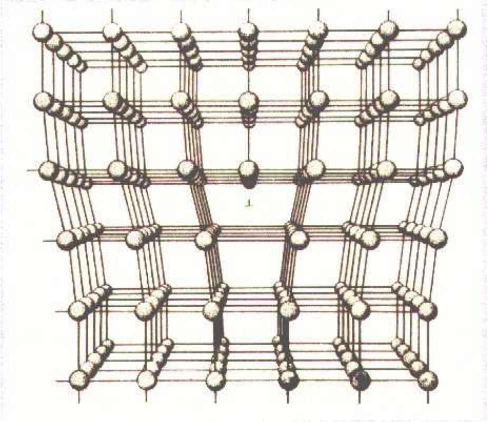
Hydrogen embrittlement of steels

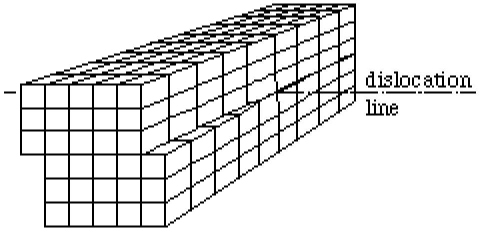
- **Hydrogen enhances the mobility of dislocations and decreases the separation distance between dislocations in a pile-up (e.g. 310S Stainless steel)**

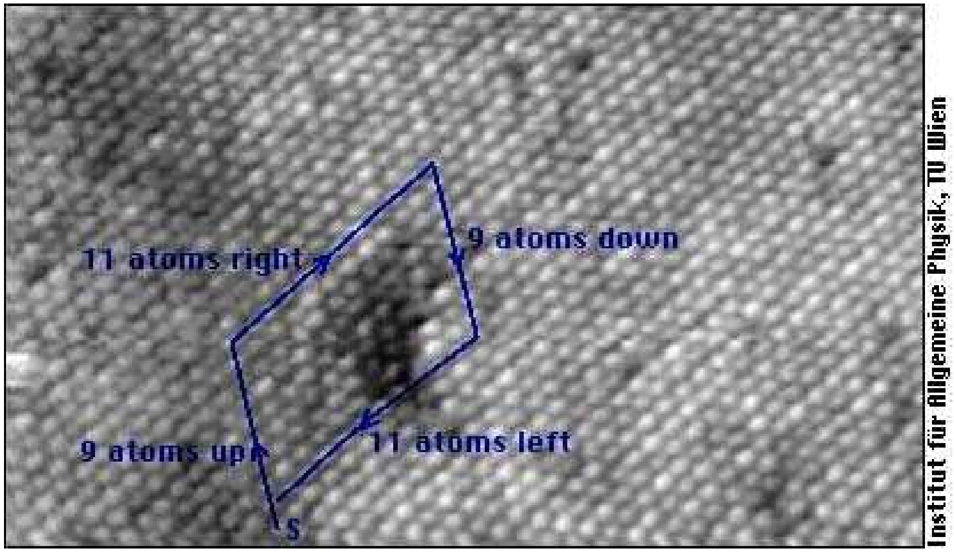


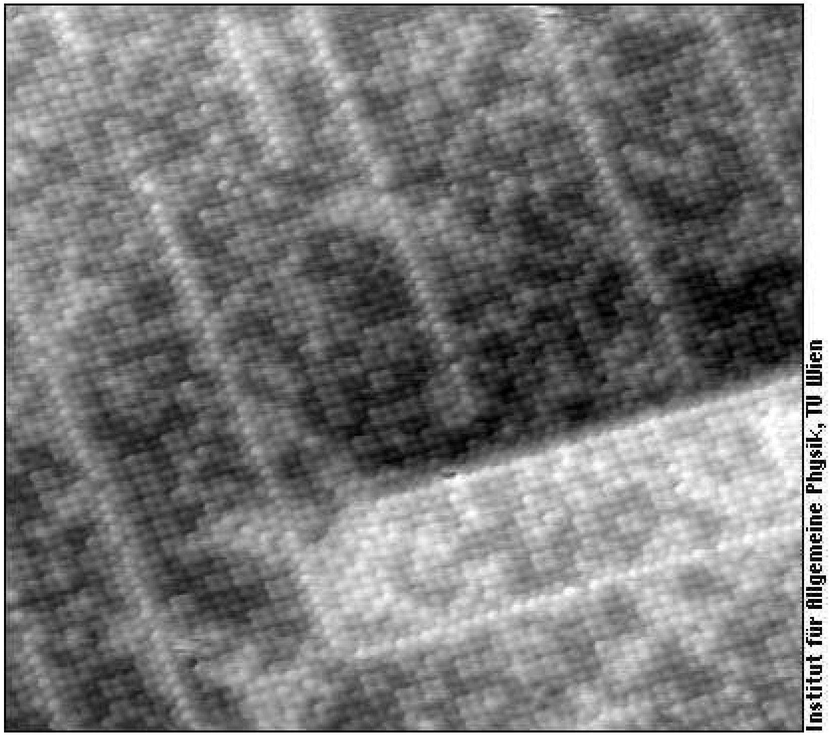
95 Torr is only 0.12 Bar

Dislocations are imperfections in the stacking of the atoms, some examples



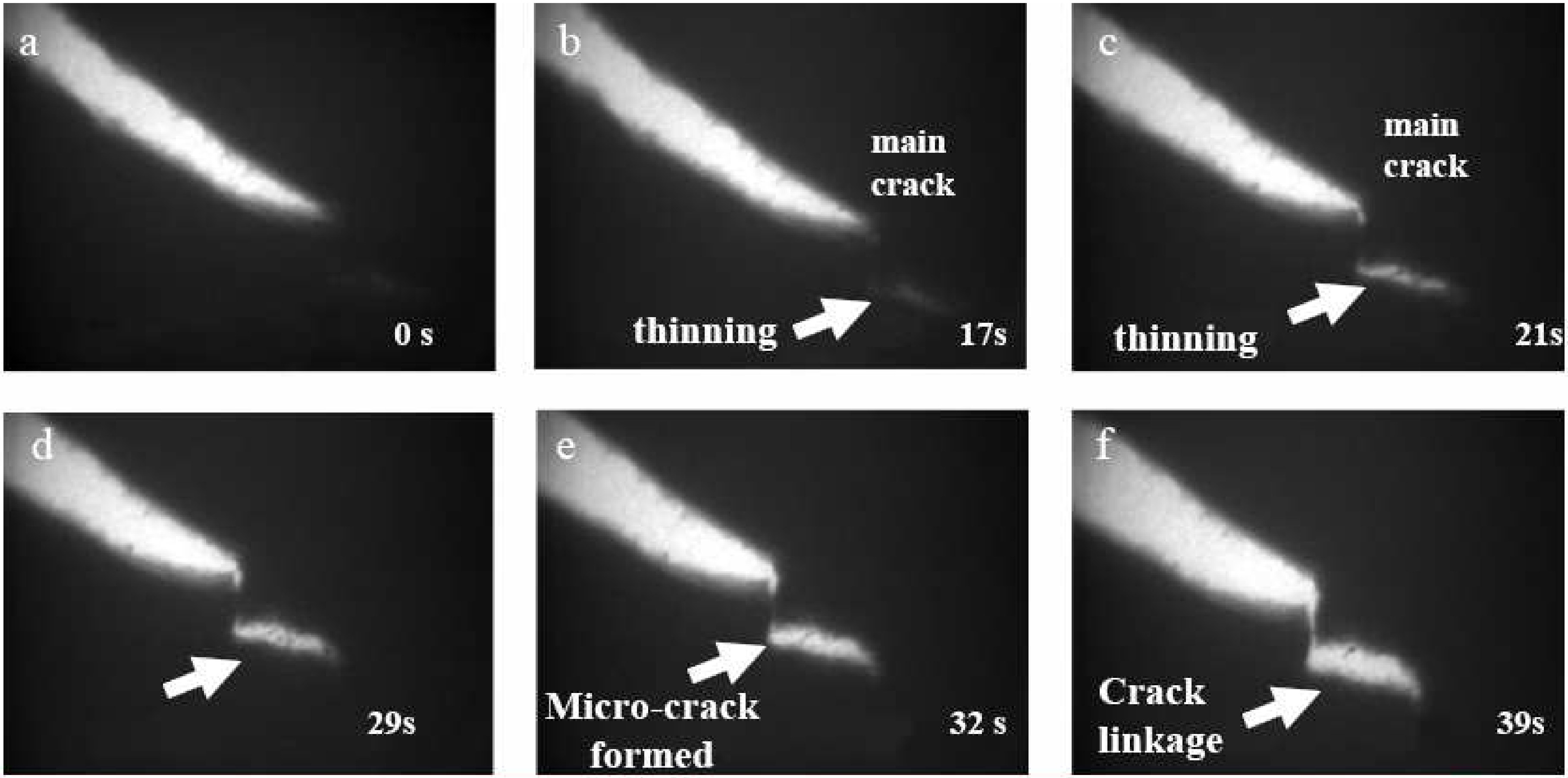






- Hydrogen enhances crack propagation rates (e.g. IN 903 system)

Static crack in vacuum. Hydrogen gas introduced →

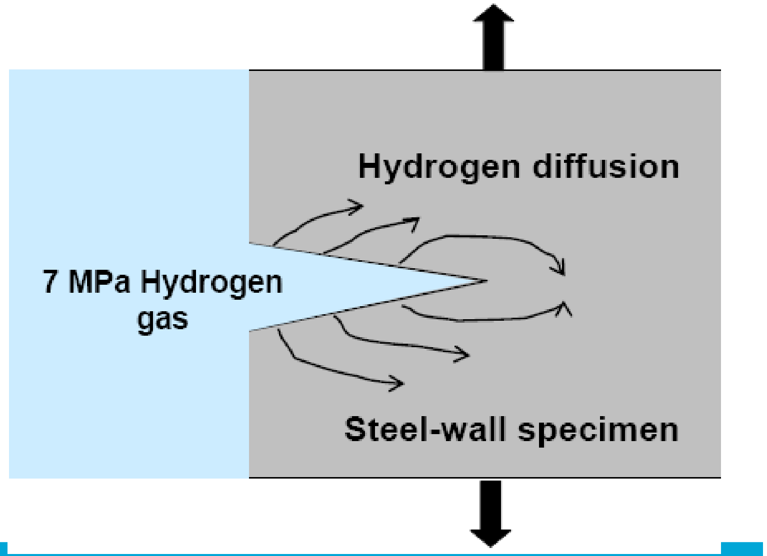


Time evolution under constant load

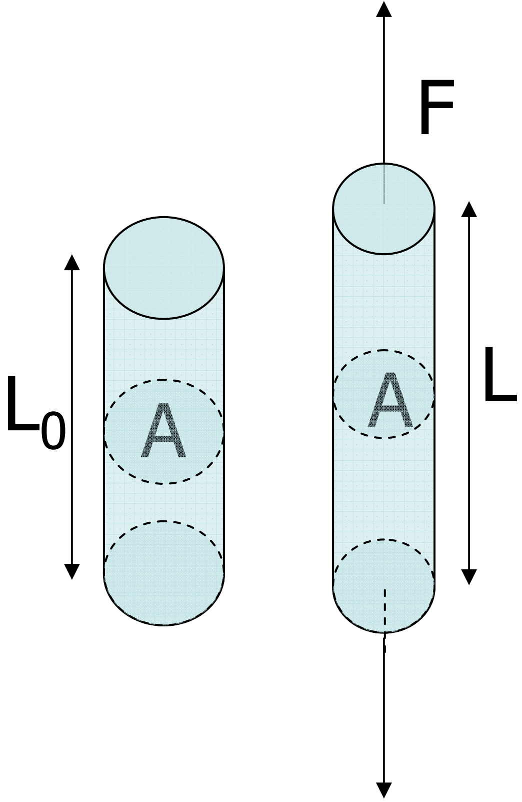
Failure mechanisms

- Hydrogen molecules can split into atoms that diffuse into the steel/metal
- they can induce enhanced mobility of the metal ions
- 2 hydrogen atoms can recombine to form H_2 gas at defects or grain boundaries already present in the material
- high pressures build up in the defects, making them grow, ultimately leading to cracks and materials failure
- some temperature treatment can dissolve the hydrogen again

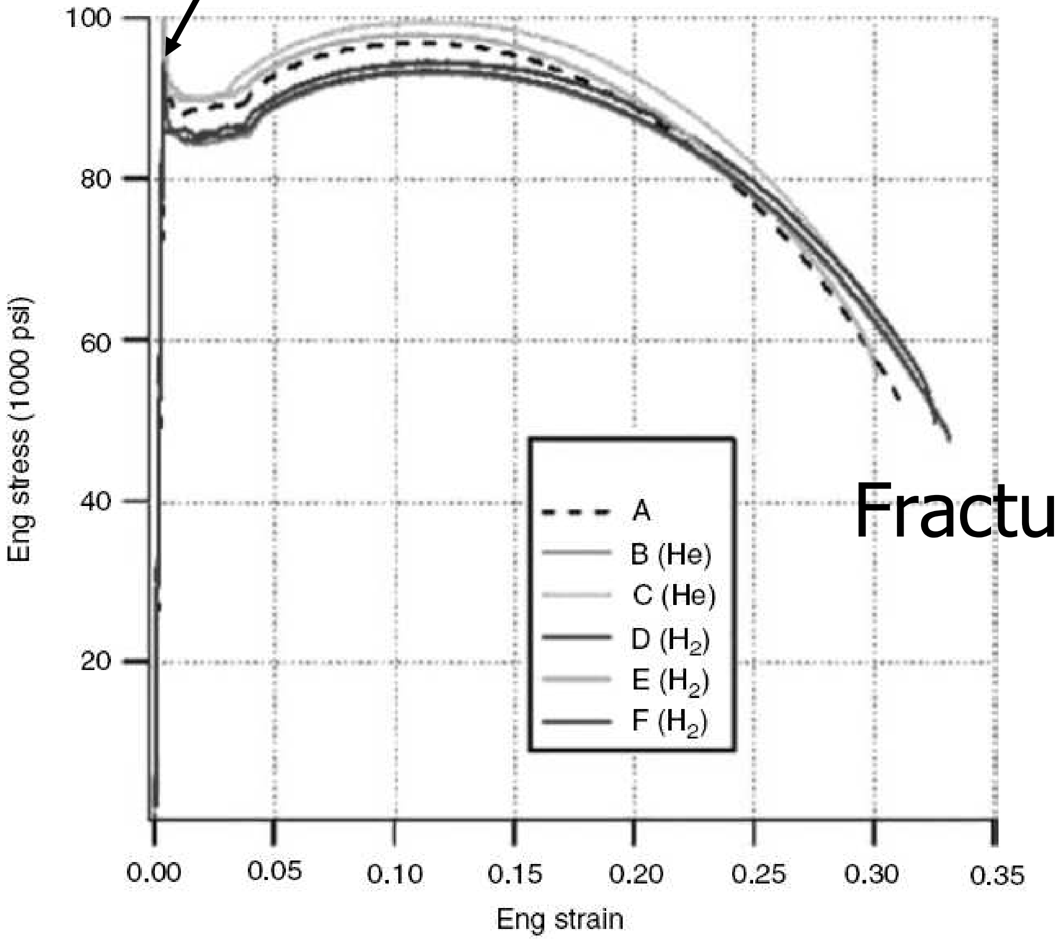
- In carbon steels also **methane** can be produced in the defects. This leads to decarburization and loss of strength and in addition the methane cannot diffuse out of the metal. This a strong **'Hydrogen attack'**.



Stress=pulling force F per surface unit of the cross section A of the rod



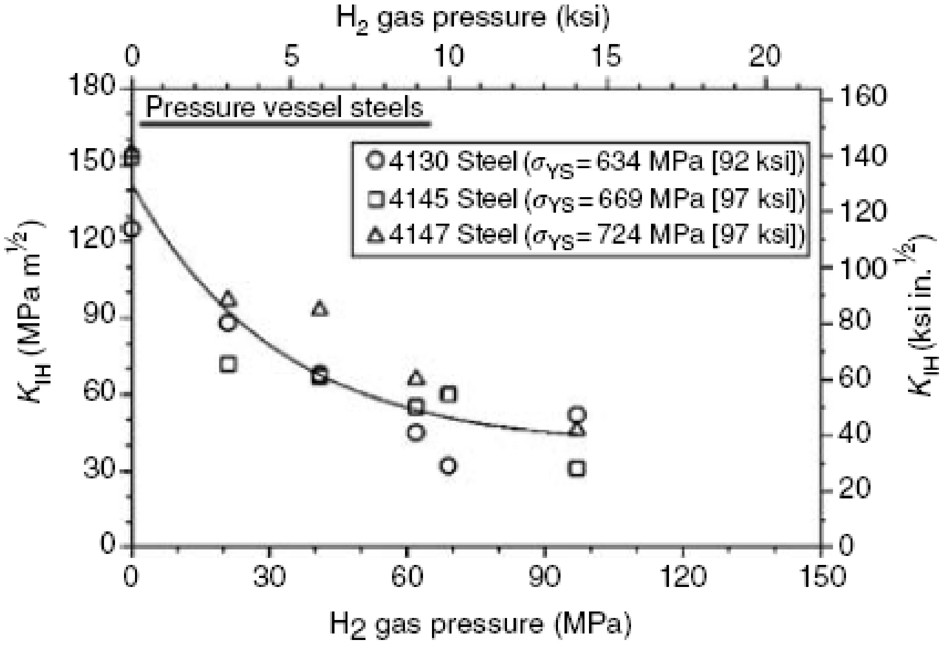
Yield stress: after this point the material is plastically deformed



Fracture

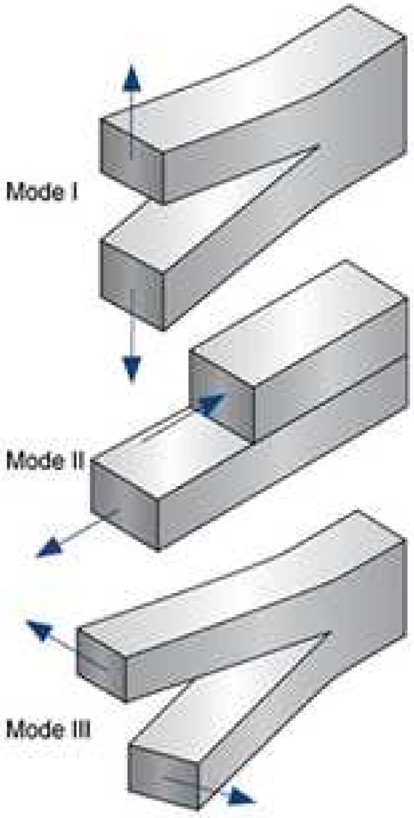
Strain = $(L-L_0)/L_0$ = elongation due to force

‘Fracture toughness’ K_I decreases upon hydrogen pressure application.
This is a parameter related to propagation of existing cracks in the ‘Mode I direction’ indicated.



(a)

$$K_I = \sigma\sqrt{\pi a \beta}$$



σ= strain
a= crack length
β= geometry factor

This fracture thoughness is an important parameter since it is assumed that there will always be microscopic fractures in construction materials, welds, …

These weakest points determine the overall failure chances.

Summary of barriers to Hydrogen Delivery using steel pipelines

– hydrogen embrittlement
– Current joining technology (welding) for steel pipelines is major cost factor and sensitive to embrittlement
– H_2 leakage and permeation pose significant challenges for designing pipeline equipment, materials, seals, valves and fittings.
– H_2 delivery infrastructure will rely heavily on sensors and robust designs and engineering.

Alternatives to metallic pipelines:

- pipelines constructed entirely or partly from polymeric composites and engineered plastics

Less costly and safer?

This is in a R&D development stage

Example of a materials science goal for plastic pipelines

Investigate feasibility of using fiber-reinforced polymer (FRP) pipeline for reduced installation costs, improved reliability, and safe operation.

Develop nanostructured plastic with dramatically reduced hydrogen permeance for use as the barrier/liner in non-metallic H_2 pipelines.

Advantages of Continuous FRP Piping

•Anisotropic characteristics of FRP piping provide extraordinary burst and collapse pressure ratings, increased tensile and compression strengths, and increased load carrying capacities.

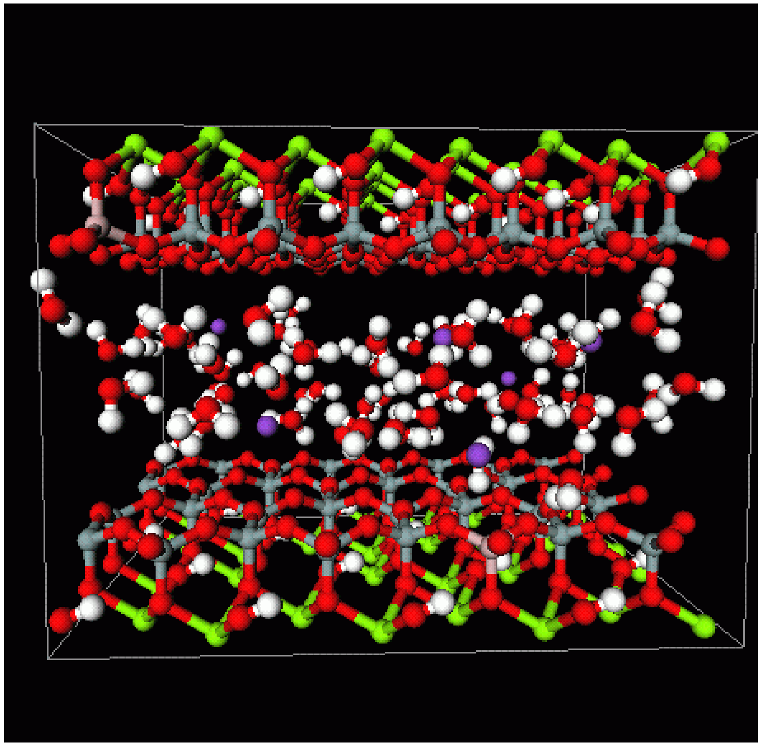
•No welding.

•Nearly jointless-many miles of continuous pipe can be installed as a seamless monolith.

•Corrosion resistant and damage tolerant.

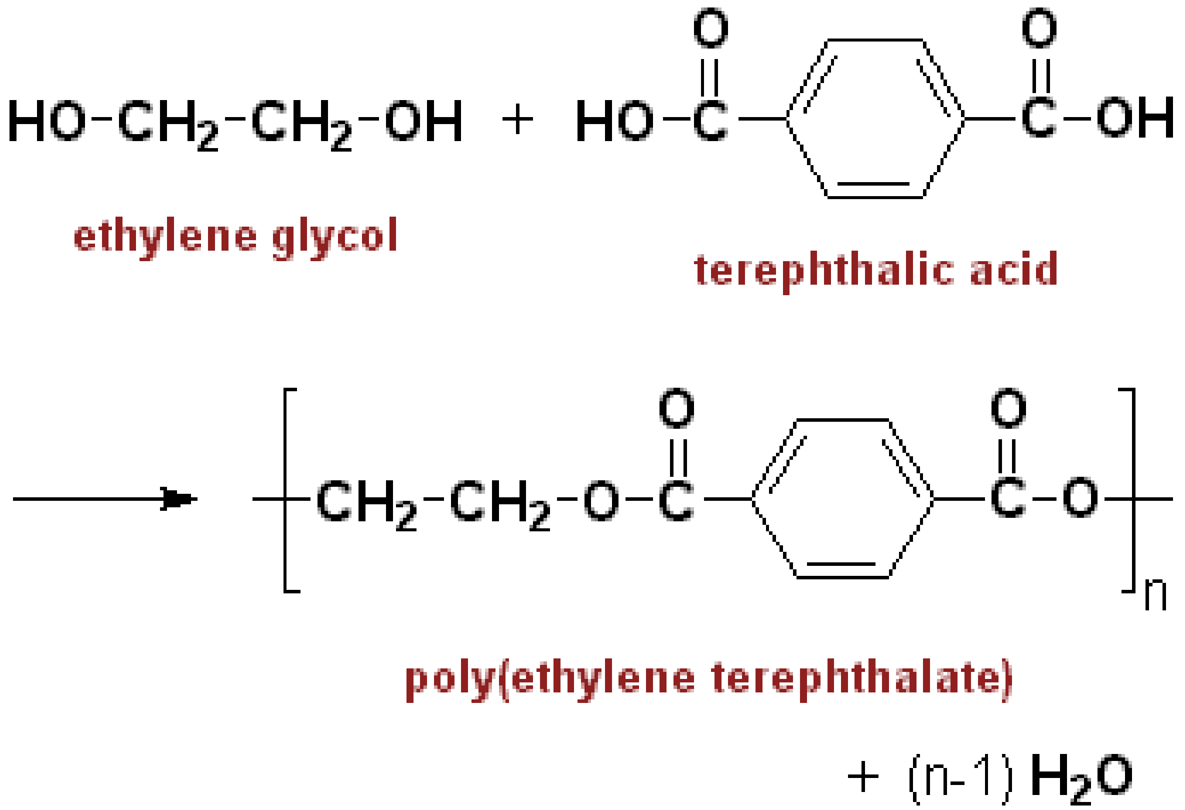
Technical development: Smart pipelines where sensors are incorporated in the walls, for monitoring state of pipeline.

Reinforcement fiber example: Montmorillonite: clay

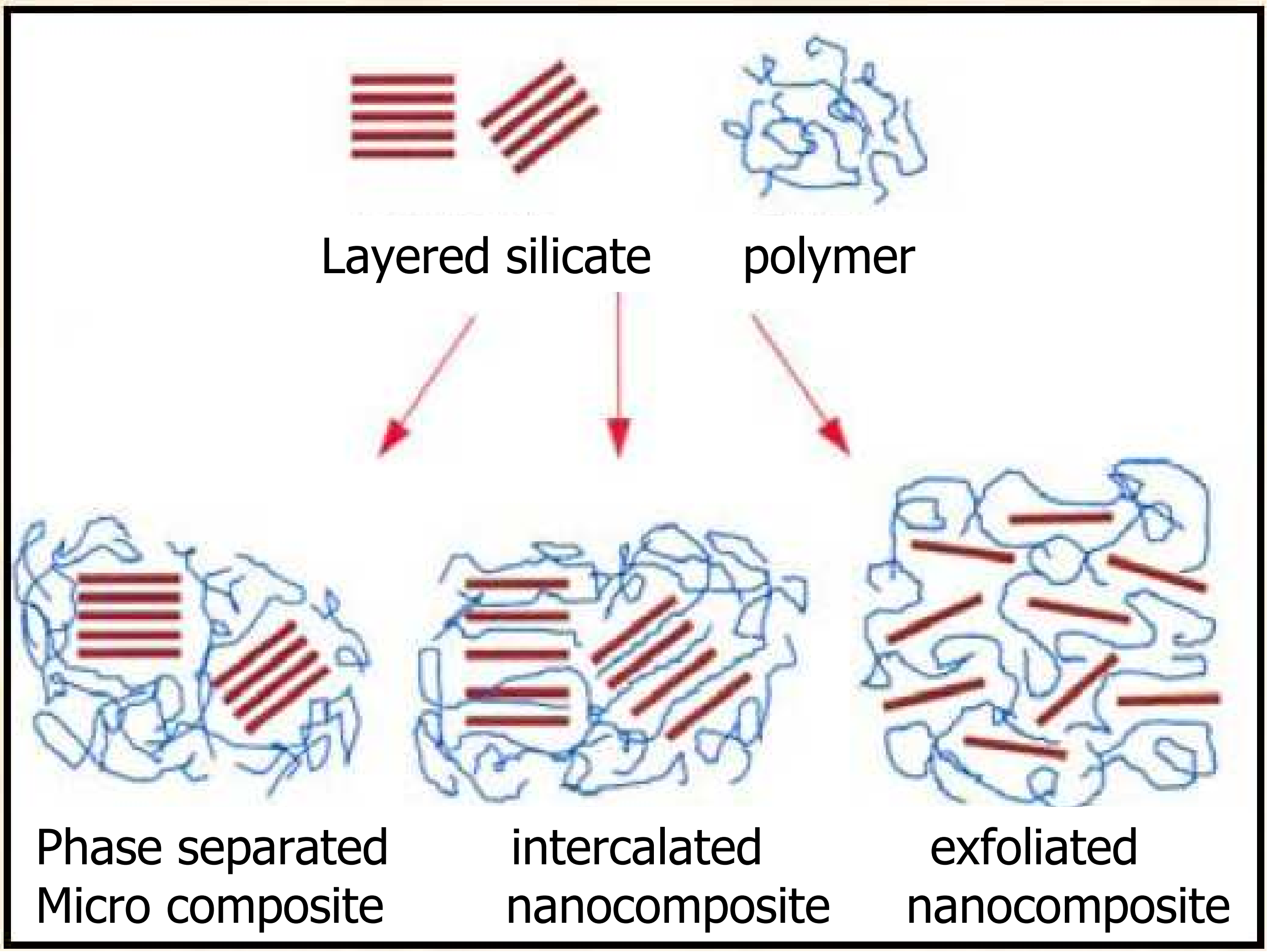


Montmorillonite: hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$.

Plastic for pipes: polyethylene terephthalate (PET)



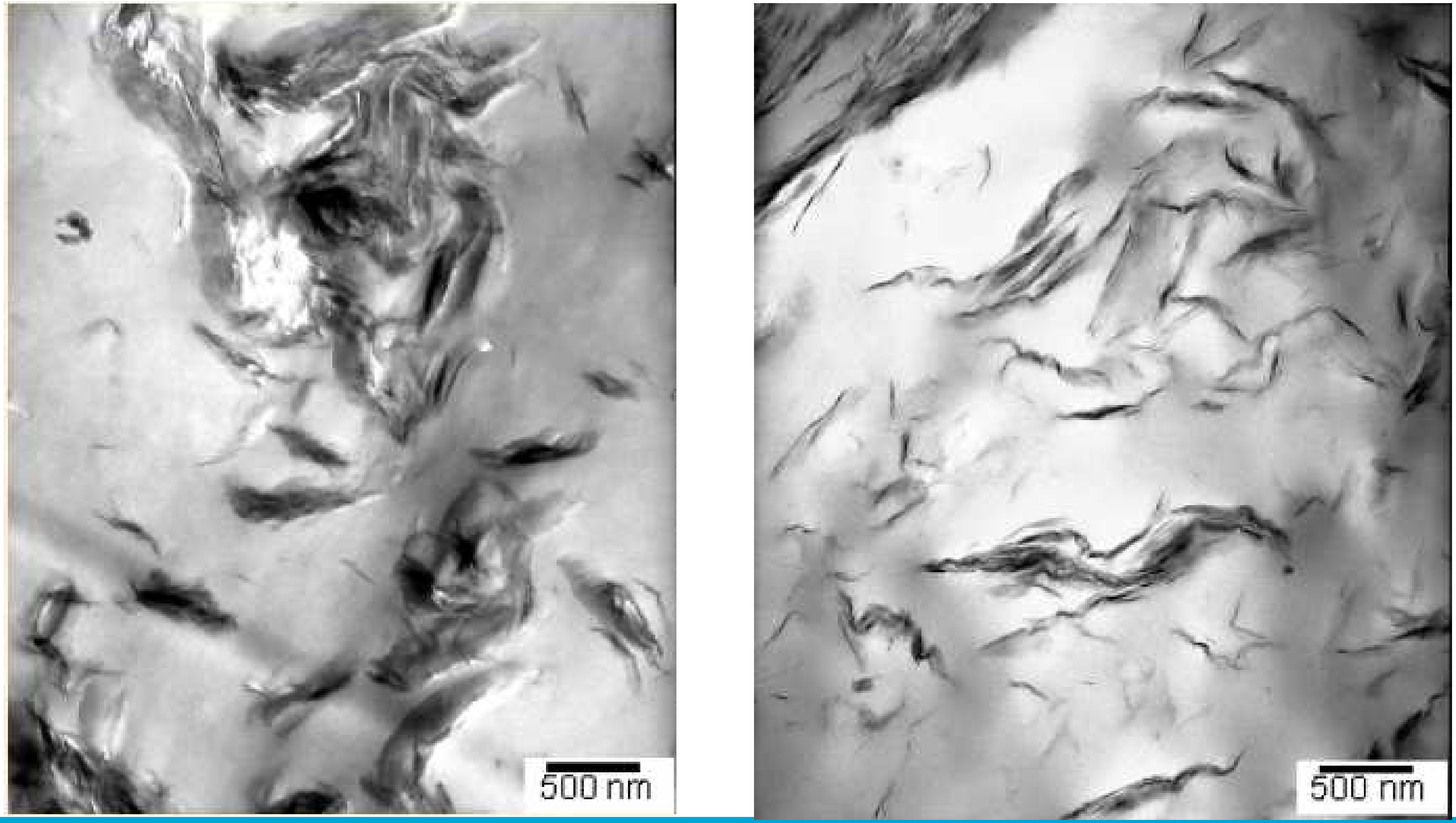
Reinforced plastic for pipes



These platelets should stop H_2 permeation

Transmission electron microscopy (TEM) of PET

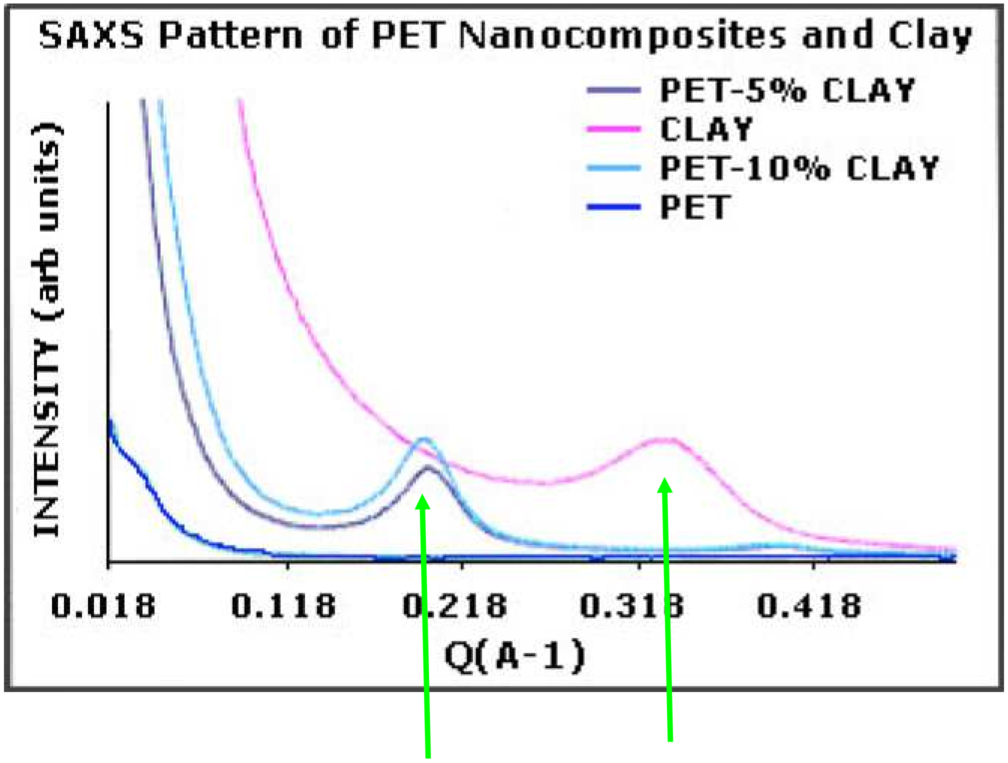
- Images of PET with 5% (left) and 10% (right) clay contents
- Clay appears as dark lines
- Most clay occurs as intercalated clusters with only partial exfoliation



Small-angle x-ray scattering (SAXS)

With this technique one can observe that:

Intercalation of PET chains increases interlayer spacing, shifting peak to lower ‘Q values’. This means that polymer goes in between plates



Interlayer distance ~ 3.1nm ~1.8nm

Hydrogen Delivery Technical Targets (2015) for pipelines (i.e. large volumes)

– Total capital cost of transmission pipelines: $800K/mile

– Total capital cost of distribution pipelines: $200K/mile

– High pipeline reliability: equivalent to today’s natural gas pipeline infrastructure

– Loss due to leakage and permeation: < 0.5% of H_2 put through pipeline

FRP Piping Feasibility Assessment (continued)

−Current capital cost (materials and installation) for 4-inch ID, 1000 PSI-rated fiber-reinforced polymer piping is $50K to $100K per mile.

−Transmitting H_2 to a population of 100,000 would require five 4-inch ID pipelines, at an approximate capital cost of $250K to $500K per mile.

−This estimate is well below the DOE 2015 target for hydrogen delivery ($800K per mile).

−However, current fiber-reinforced piping needs liner with acceptably low hydrogen permeation and needs qualification for high-pressure H_2 service. (this liner could still mean a thin steel inner wall, Fig 10.17 Gupta)

Transport of hydrogen requires compression

… and so does storage of H_2

Compression of hydrogen gas

In order to evaluate the costs of compression we need to determine the temperature and pressure effects of compression of a gas

- ideal gas law: PV = nRT
- Internal energy of a gas:

$$U = \sum_i W_{molecule,i} = nN_A \langle W_{molecules} \rangle = nN_A \frac{\nu}{2} kT = n \frac{\nu}{2} RT$$

- With n the number of moles of molecules and ν the number of internal degrees of freedom of the molecule involved. One would expect that ν equals roughly 3 times the number of atoms in the molecules (each atom in the molecule can move in 3 directions). He: 3, H_2: 6, CH_4: 15. However, due to the electrons the atoms have some finite size and e.g. He can therefore also spin.

This can lead to more degrees of freedom. In addition ν can be T dependent.

H_2 hot enough to ionise and become up to 4 particles (2 protons + 2 electrons)

H_2 behaves as two rigidly connected particles, i.e. 5 (3 translations, 2 rotations)

Table 2.2

Ratio of the Specific Heats of Some Monatomic Gases

Gas	Temp. (K)	γ
Helium	93	1.660
Argon	298	1.668
Krypton	298	1.68

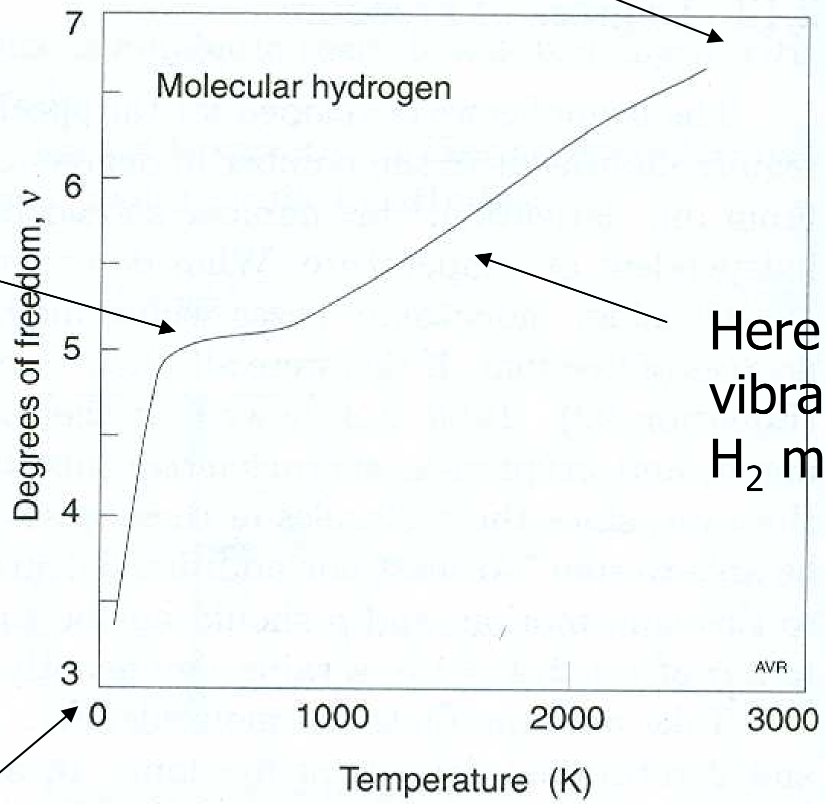


Figure 2.4 The number of degrees of freedom of molecular hydrogen as a function of temperature.

Here also vibrations inside H_2 molecule: 6

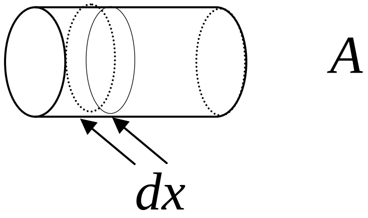
H_2 behaves as single particle, i.e. only 3

Compression of hydrogen gas

- Specific heat per mole at constant volume: $$c_V = \frac{1}{n}\frac{dU}{dT} = \frac{\nu}{2}R$$

unit : $JK^{-1}mol^{-1}$

- Work done by a moving piston: $dW = pAdx = pdV$, so $W = \int PdV$



- Specific heat at constant pressure c_P : this equals c_V plus the d work/dT delivered by the piston upon temperature expansion when T is raised:

$$\frac{1}{n}\frac{PdV}{dT} = \frac{P}{n}\frac{d}{dT}\frac{nRT}{P} = R$$

so $$c_P = c_V + R = \frac{\nu}{2}R + R = \left(1 + \frac{\nu}{2}\right)R$$

$$\gamma = \frac{c_P}{c_V} = \frac{R(1+\nu/2)}{R\nu/2} = 1+\frac{2}{\nu}$$

So for larger numbers of degrees of freedom there is less difference between the constant volume and constant pressure specific heat.

‘**Adiabatic compression**’: no heat exchange between gas and environment
$W=F_1(h_0-h_1)$ with F_1 the constant force and h_0 and h_1
the differences in piston position. All of W put into the gas:

$$W = \Delta U = F_1(h_0-h_1) = P_1A(h_0-h_1) = nc_V(T_1-T_0)$$

also

$$T_1 = \frac{P_1V_1}{nR} = \frac{P_1Ah_1}{nR} = \frac{F_1}{nR}h_1$$

same energy change, but now caused by a T difference at constant V

Then $$F_1(h_0 - h_1) = \frac{c_V}{R} F_1 h_1 - n c_V T_0$$

And solving for h_1 $$h_1 = \frac{\gamma - 1}{\gamma} \left(h_0 + n c_V \frac{T_0}{F_1} \right)$$

and $$F_1 = \frac{n c_V T_0}{\frac{c_V}{R} h_1 - (h_0 - h_1)}$$

So we know for adiabatic conditions a constant force $F1$, pressure P_1 the resulting volume from Ah_1 and the temperature T_1 reached.

For **isothermal conditions**: $PV=P_0V_0$ so $P=P_0V_0/V$

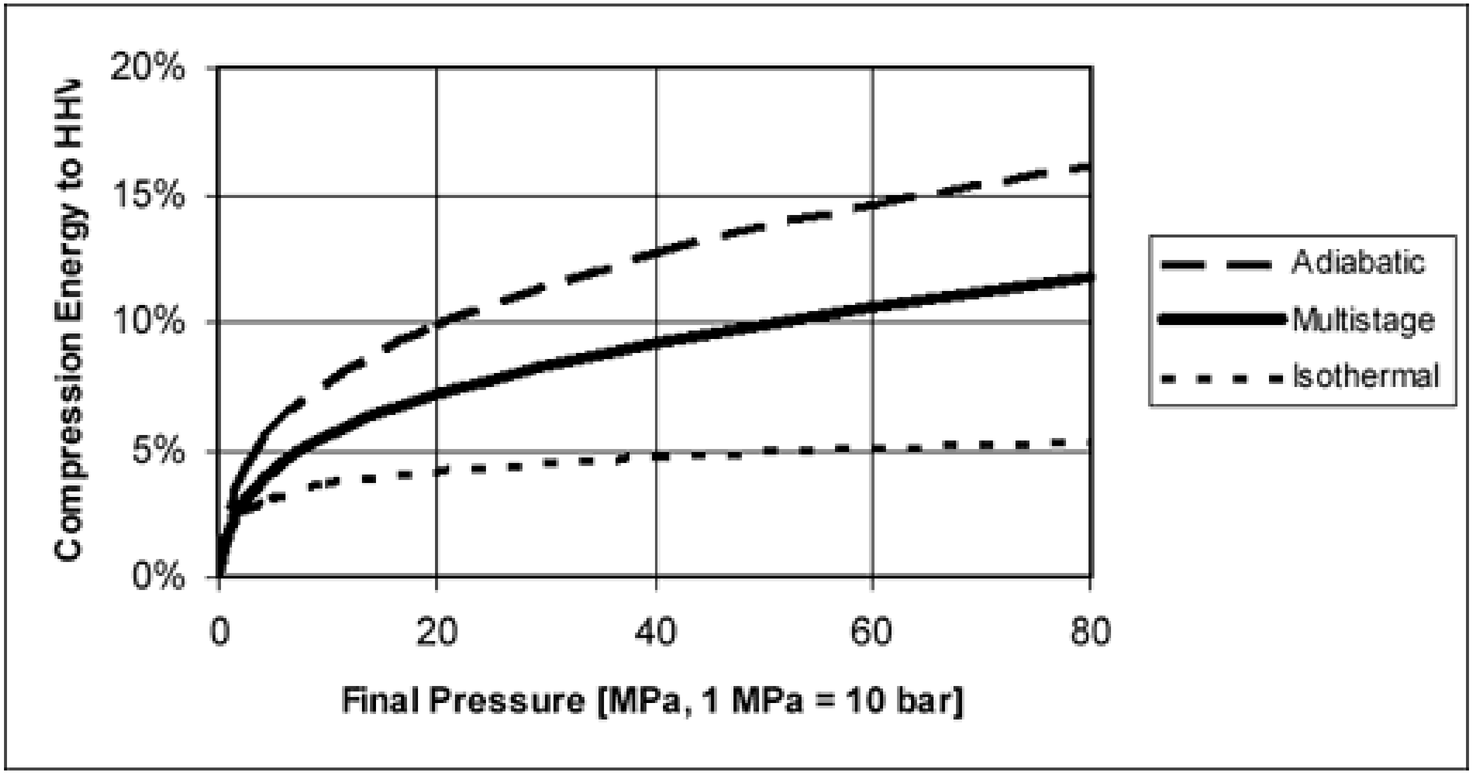
$$W=\int_{V_0}^{V_1} PdV = P_0V_0\int_{V_0}^{V_1}\frac{dV}{V} = P_0V_0\ln\frac{V_1}{V_0} = P_0V_0\ln\frac{P_0}{P_1} = nRT\ln\frac{P_0}{P_1}$$

The work done on the gas to compress towards the same volume is much less under isothermal conditions than under adiabatic conditions because the pressure remains much lower in the isothermal case: there is no T raise.

But: in general isothermal compression is hard to realize, because the required cooling is too slow.

Compression of hydrogen gas

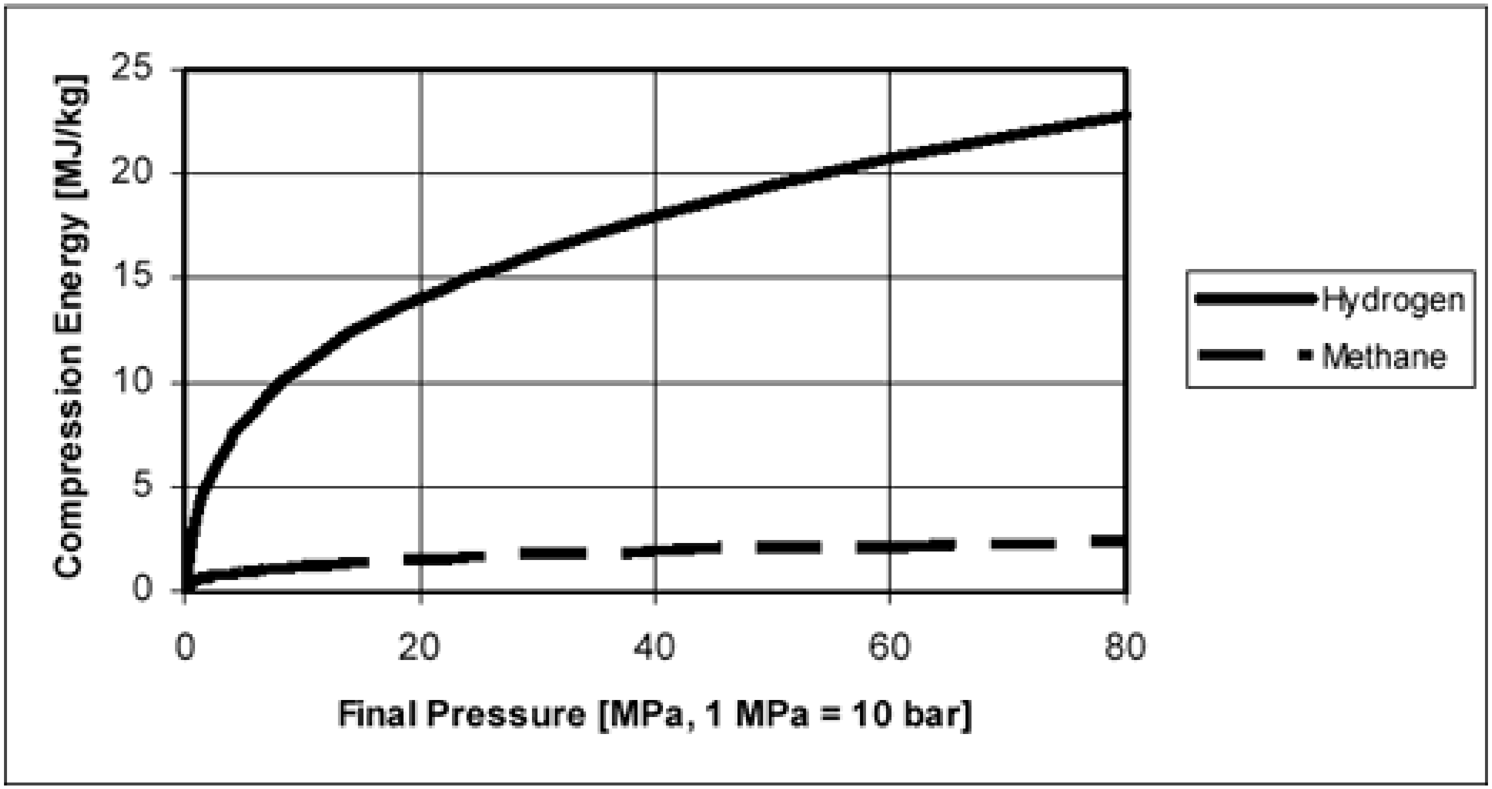
After cooling the adiabatically compressed gas to the same T as the isothermal compressed gas, the same compressed hydrogen product results.
Difference in energy during compression expressed in % of the higher heating value of the H_2 gas:



Compression of hydrogen gas

For the same volume change the force F_1 depends on C_V. Larger C_V means less heating of the gas, lower pressure and therefore less force.
Because for hydrogen the number of degrees of freedom of the gas is lower than for methane, C_V is lower, so more energy is needed for compression.

$$c_V = \frac{\nu}{2} R$$



However, the units are MJ/kg, so one should also look to the

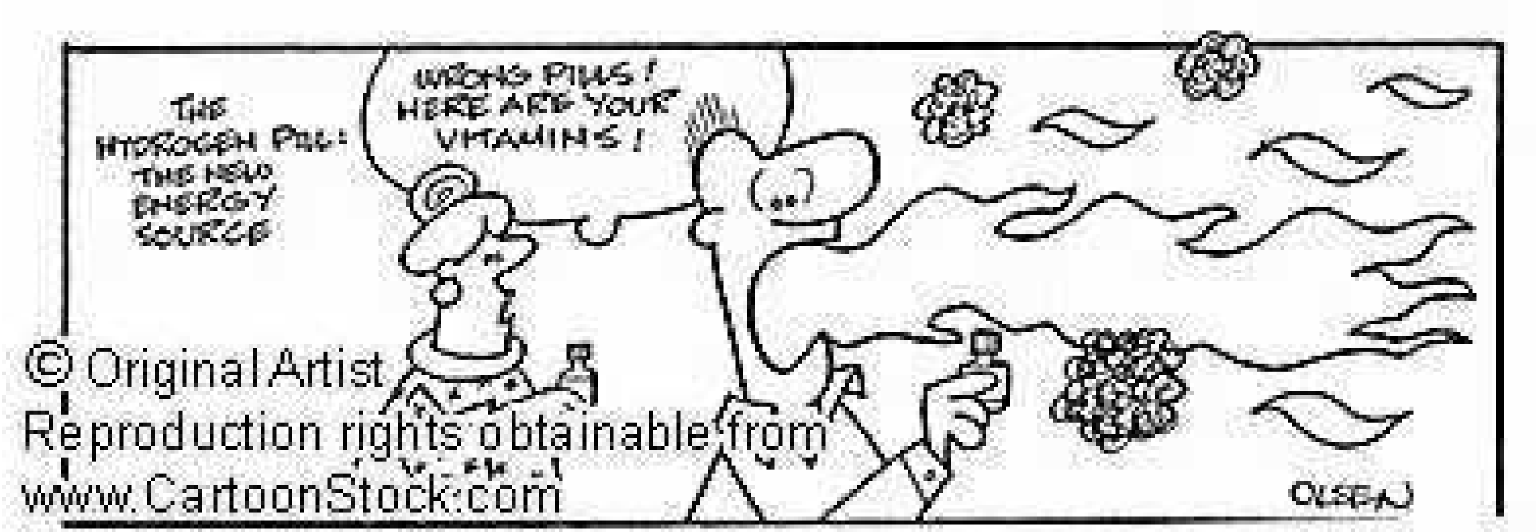
		H_2	CH_4
Gravimetric HHV	MJ/kg	142.0	55.6

This decreases the difference between CH_4 and H_2 in compression costs as HHV % but still a factor ~3 remains.

Hydrogen transport and storage

- gas cylinders
- liquid
- Pipelines
- metal hydrides
- surface adsorption materials

Needs compression



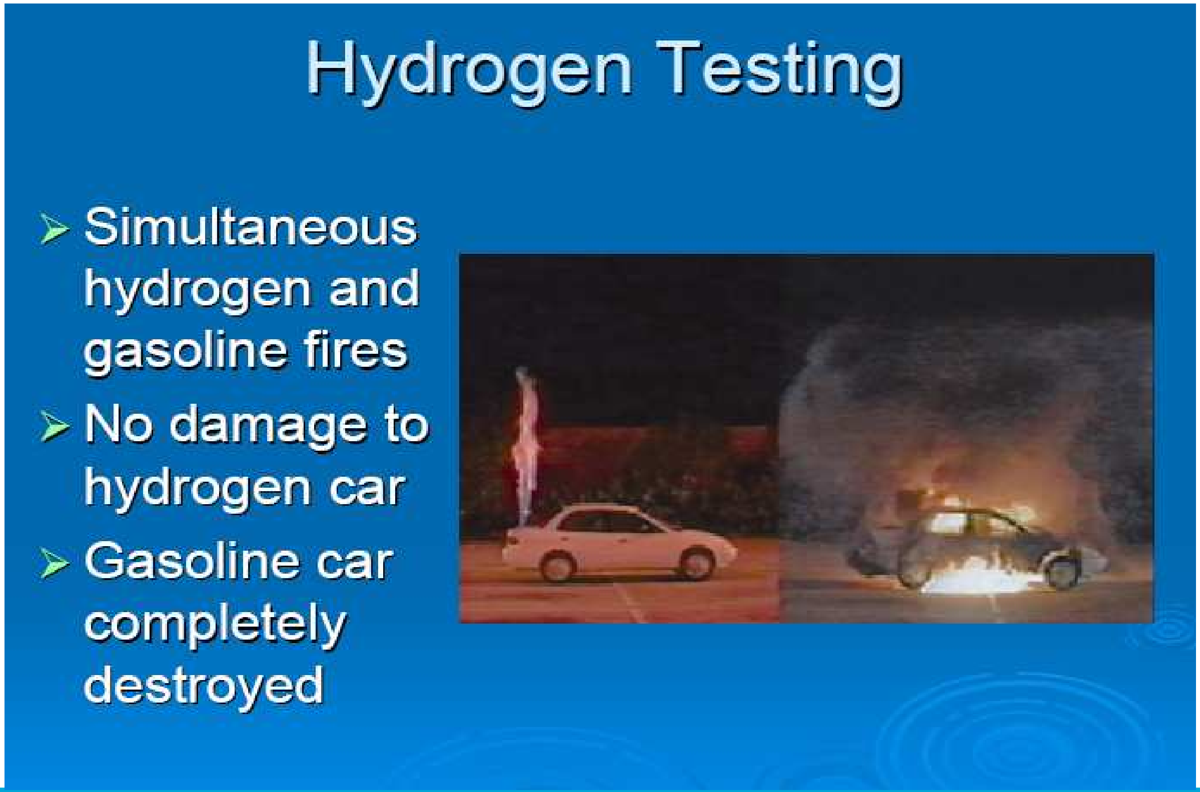
Containers for compressed hydrogen gas

The target that industry has is a 70 MPa cylinder with a mass of 110 kg resulting in a gravimetric storage density of 6 wt.% and a volumetric storage density of 30 kg m^{-3}.

Example: fiber laminated tank
Operating P: 650 Bar
Burst P: 1800 Bar
Cycle life: 12500 cycles

Safety

- The high pressure calls for containers that are safe.
- containers are designed to leak first and not explode first.
- test pressures are always far above operating pressures (3x).
- Different types of crash test are performed for cars



Hydrogen Testing

- Simultaneous hydrogen and gasoline fires
- No damage to hydrogen car
- Gasoline car completely destroyed

Extensive Research

Bonfire Test

Crash Tests

Assessment after Drop Test

Vibration Test

Permeation Test

Concluding remarks for compression of hydrogen gas

- compression needs significant energy compared to higher heating value energy content

- hydrogen as light diatomic gas has a low specific heat, which makes compression less easy

- High pressures are needed to reach sufficient H_2 density. Tests with busses are running using 350 Bar. Future aim: 750 Bar.

- When compressed, the gas can be loaded rapidly from one tank in another. Rapid loading of e.g. car tanks will be feasible.

- Public acceptance of a 750 Bar tank is an important issue.

H-Storage: Liquid H_2

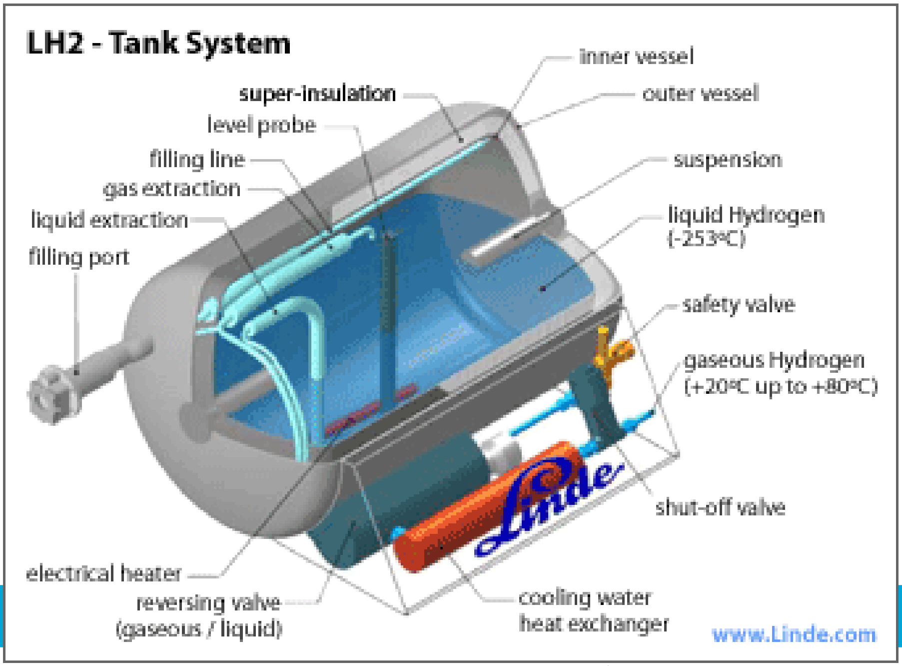
>100 years ago James Dewar succeeded in the first liquefaction of hydrogen. Also inventor of thermos (vacuum insulated) flask

Advantage compared to pressurizing: No high pressures
Higher energy density (compared to 800 bar H_2)

Disadvantage: Low temperatures 20.4 K (-253 °C)

Issues of liquefaction:

(1) Costs liquefaction
(2) Costs tank system
(3) Boil off (loss of H_2)



Liquid H_2, Application realised to date, example

BMW: Running on hydrogen, the 745h produces 184 horsepower and can achieve a top speed of 133 mph. The cruising range is 190 miles. Added to the 400-mile range of the normal fuel tank, the 745h can go 600 miles between fill-ups.

Application where light liquid H_2 could be necessary: future hypersonic airplanes

- Lockheed investigated airplane for 234 passengers that could reach Mach 2.7 for 7800 km range.

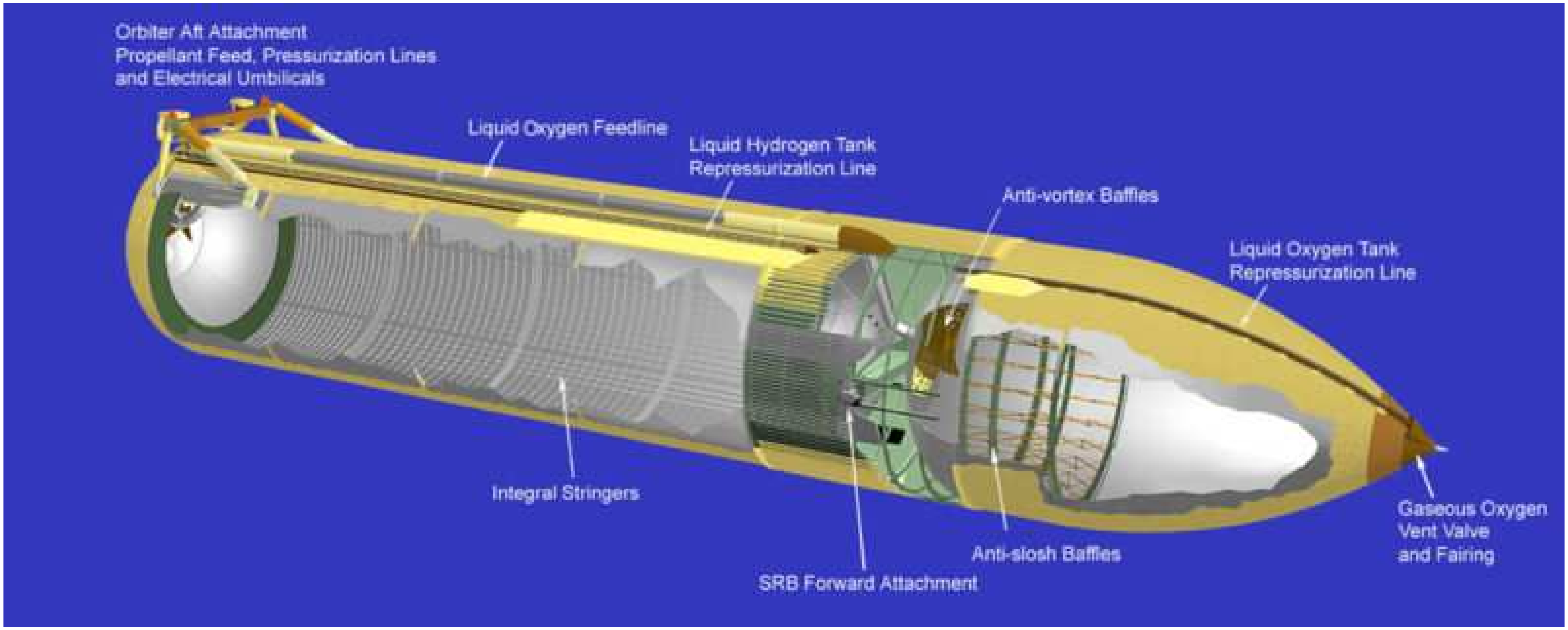
Weight of kerosene powered aircraft: 232 tons of which 72 tons would be fuel.

Hydrogen powered aircraft: 169 tons of which <22 tons would be fuel

- Proposed ‘space plane’: Mach 8, capable of balistic/orbital flights

Largest liquid hydrogen user for propulsion: Space Shuttle

Cape Canaveral storage unit: 3375 m^3, 240 tons H_2, 34 TJ




Discovery

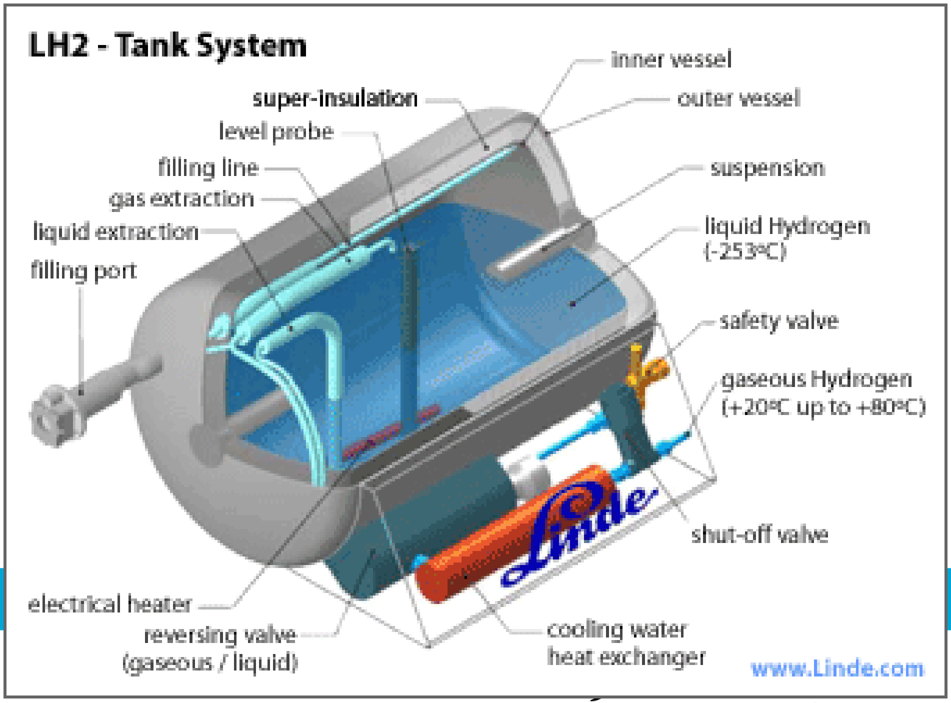
Hydrogen boil off

Liquid hydrogen storage systems lose some hydrogen gas by boil-off.

This is due to unavoidable heat leakage, and must be permitted for safety (pressure build up)

For small storage tanks it can go up to 3 to 4 per cent a day, meaning about 50 to 60 % for two weeks parking!

Quantum mechanical property that promotes boil off: Ortho and Para H_2

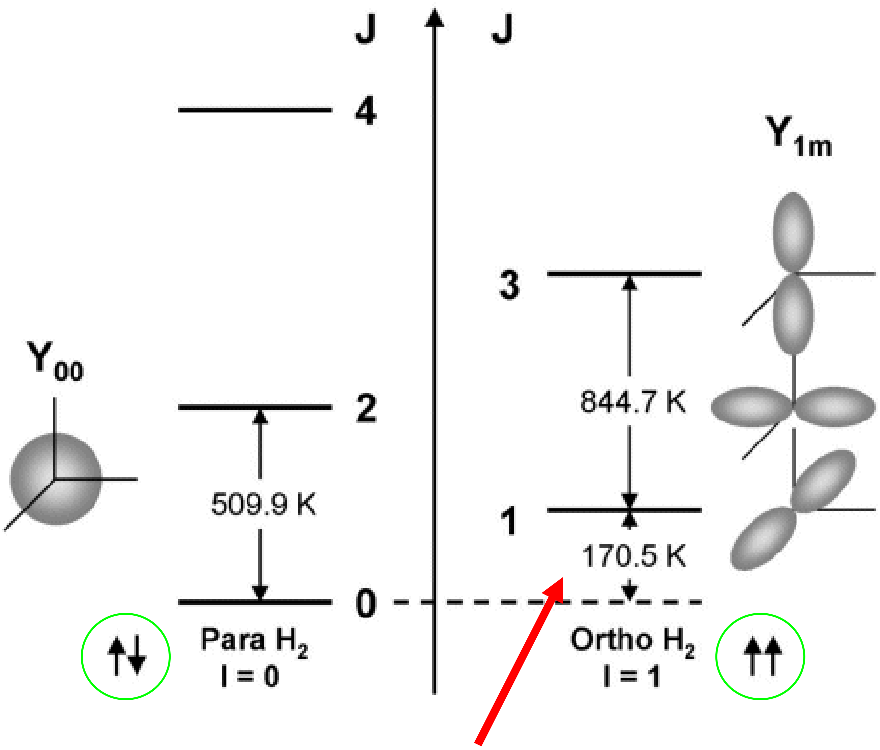


Ortho and Para hydrogen: fundamental quantum mechanics

Two different types of diatomic hydrogen:
Ortho: nuclear proton spins parallel
Para: nuclear proton spins anti-parallel

Ortho-H_2 is an exited state of hydrogen and Para-H_2 the ground state (lowest energy state)

Quantum mechanics says that fermions (half integer spins, like the proton I=1/2) need to have an ‘anti-symmetric wave function’ with regard to exchange of the protons. Hence Para-H_2 only displays symmetric rotational states (J: even) and vice versa



Note: 170K per molecule is a large amount of energy!! The latent heat of evaporation is only ~ 445kJ/kg ~ 25K/H_2.

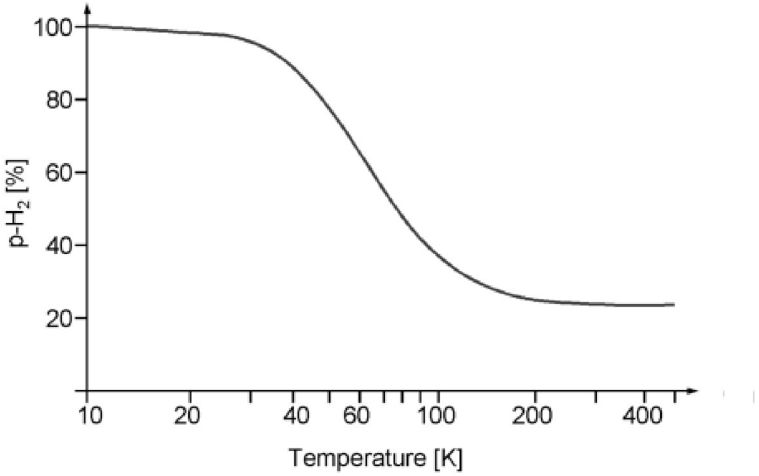
Ortho and Para hydrogen

Equilibrium ratio between Para-H_2 and Ortho-H_2 depends on temperature. The conversion from Ortho to Para is very slow, because it is depending on weak nuclear magnetic interactions.

Rapidly condensed H_2 contains a larger than equilibrium fraction of Ortho. The (slow) conversion from Ortho to Para is exothermic, and the heat (170 K/H_2) that is released evaporates the liquid hydrogen!

Without catalyst for ortho to para conversion:
First hour: evaporation loss 1%
First week: 50% is lost

Para-H_2 percentage



Hence, in practice it is important that for producing liquid H_2, all of it is in the Para form, which is realized in practice by leading the cold H_2 gas across paramagnetic catalysts (e.g. Fe or Ni compounds)

Liquefaction of hydrogen

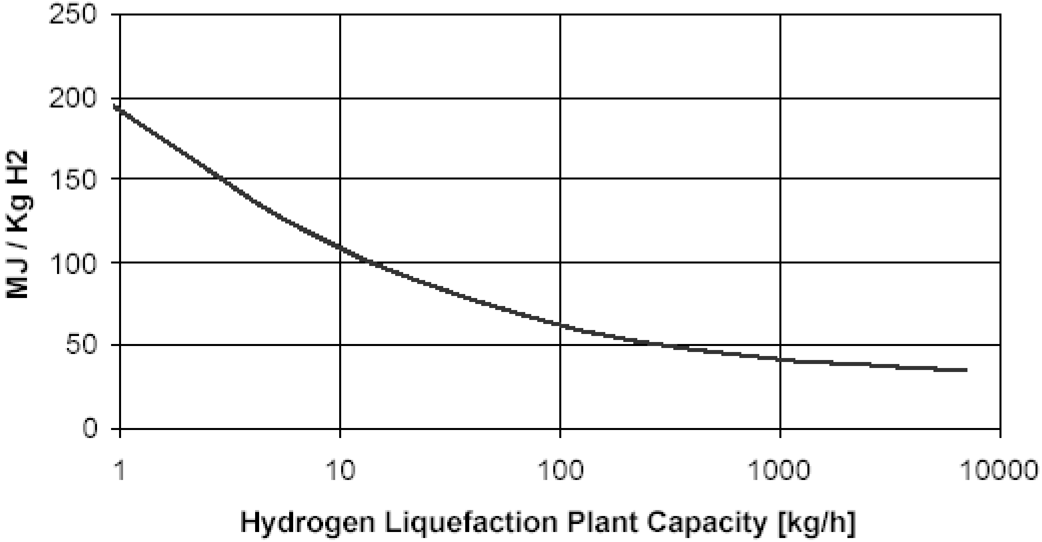
The cooling is accomplished by multi-stage compression and expansion coupled with counter-flow heat exchange and energy recovery by expansion turbines.

Energy needed to cool an ideal gas:
$\Delta U = c_p(T_2 - T_1)$

14.2 MJ/kg theoretically for cooling H_2 from 298 K to 20.4 K this is about 10% of the energy content of H_2 (140 MJ/kg)

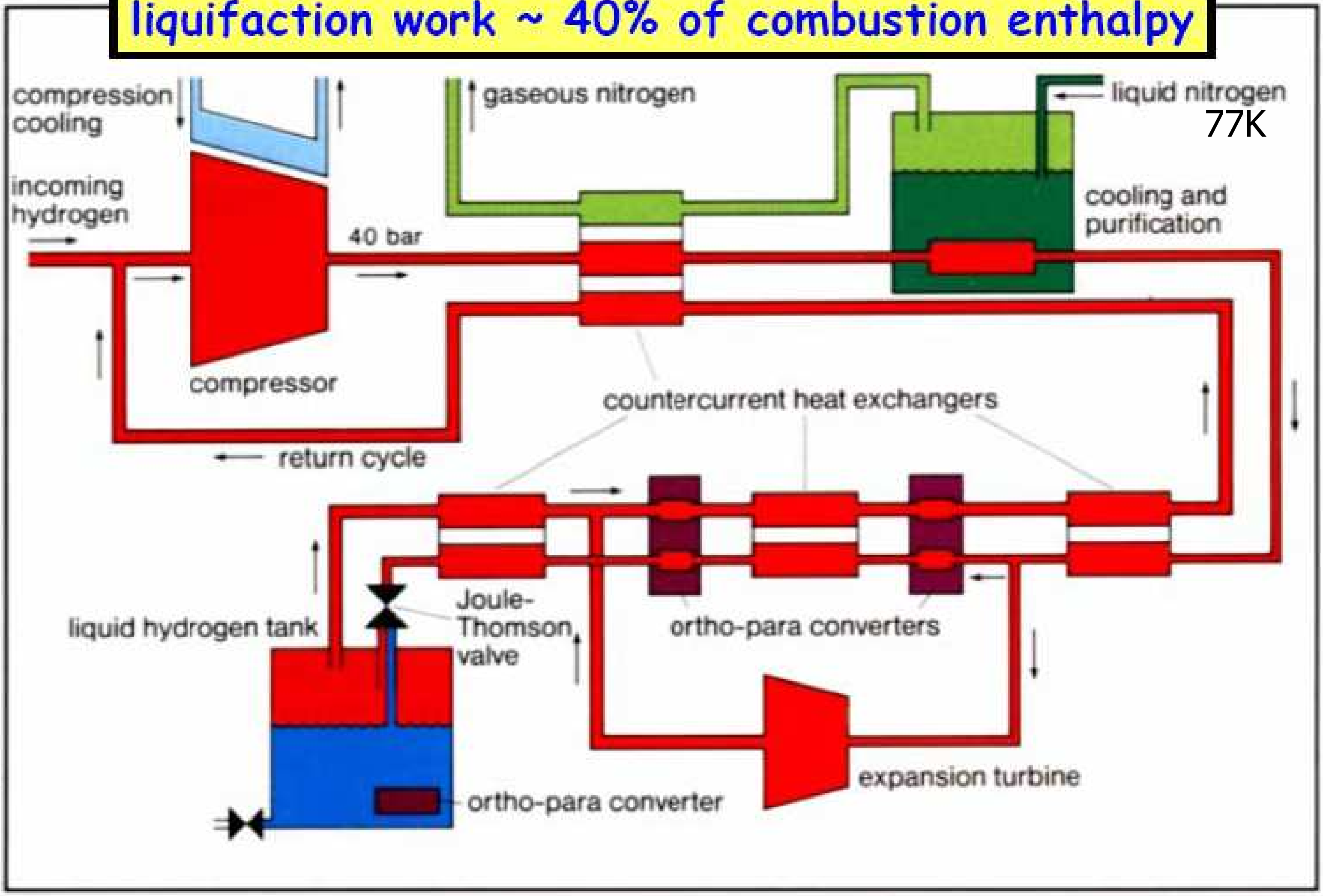
In practice there are more losses related to the cooling: electrical, mechanical, thermal, and flow-related losses: 40 MJ/kg is quoted in practice

Energy costs depend strongly on capacity of a liquefaction plant, but never comes below ~30 %:



Liquifaction of hydrogen

liquifaction work ~ 40% of combustion enthalpy



Gas expansion and cooling

Expansion of hydrogen gas leads to cooling if:

- the gas performs work on a piston during the expansion

- or the temperature is below the ‘inversion temperature’.
The latter is a result of the increased distance between the interacting molecules → increased potential energy → reduced kinetic energy → reduced temperature.

Hydrogen has a maximum inversion temperature of 205 K. For this reason pre-cooling is necessary if expansion without a piston is used (e.g. through a valve into a fixed volume).

Why heating above inversion T? At high T there are more collisions between the molecules. During collision → at higher potential energy → lower kinetic energy/T. Upon expansion → less collisions → on average lower potential energy → higher kinetic energy i.e. higher T

Conclusions liquefaction H_2

Large energy losses liquefaction

Boil off leads to loss of fuel

Expensive tank technology

Still relatively small energy density

High purity H_2 required because all contaminants freeze (blockage of system hazard)

Ortho H_2 needs to be converted to para H_2 before storage to reduce loss

Sustainable Hydrogen and Electrical Energy Storage